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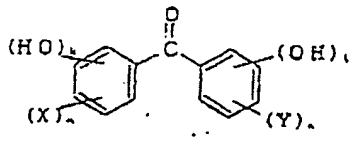
Applicant: Pierce Co. Ltd.

Title of the Invention:

MICROCAPSULES INCLUDING AN ULTRAVIOLET ABSORBER, METHOD FOR MANUFACTURING THE SAME, AND COSMETICS CONTAINING THE MICROCAPSULES

Claims:

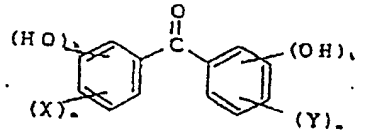
1. Microcapsules including an ultraviolet absorber, characterized in that, a benzophenone derivative represented by the formula



(in the formula, X in the number of m and Y in the number of n each is same or different and each is a C_{1-24} alkyl group, alkoxy group, sulfonic acid group or an alkaline metal salt thereof; m and n each is an integer of 0-3; and the sum of k and l is an integer of 1-4) is included in spherical fine particles being mainly composed of silica and having an average particle size of 0.1-30μm.

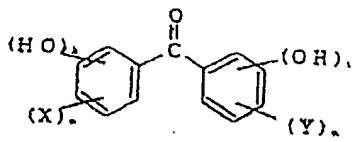
2. A method for the manufacture of microcapsules

including an ultraviolet absorber, characterized in that, a benzophenone derivative represented by the formula



(in the formula, X in the number of m and Y in the number of n each is same or different and each is a C_{1-24} alkyl group, alkoxy group, sulfonic acid group or an alkaline metal salt thereof; m and n each is an integer of 0-3; and the sum of k and l is an integer of 1-4) is dissolved in an aqueous solution of alkaline metal silicate, the aqueous solution is mixed with an organic solvent having a solubility of 5% or less to the above benzophenone derivative and water to prepare a water-in-oil type emulsion, then an acidic aqueous solution which is able to produce a water-insoluble precipitate by a neutralization reaction of the above alkaline metal silicate and the benzophenone derivative dissolved in an alkali and, after that, filtration, washing with water and drying are carried out if necessary whereby the said benzophenone derivative is included in spherical fine particles being mainly composed of silica and having an average particle size of 0.1-30 μm.

3. A cosmetic agent, characterized in that, microcapsules including an ultraviolet absorber where a benzophenone derivative represented by the formula



(in the formula, X in the number of m and Y in the number of n each is same or different and each is a C_{1-24} alkyl group, alkoxy group, sulfonic acid group or an alkaline metal salt thereof; m and n each is an integer of 0-3; and the sum of k and l is an integer of 1-4) is included in spherical fine particles being mainly composed of silica and having an average particle size of 0.1-30μm are contained therein.

Detailed Description of the Invention:

(Technical Field of the Invention)

The present invention relates to microcapsules where an ultraviolet absorber is included therein, to a method for the manufacture of the said microcapsules, and to a cosmetic agent containing the said microcapsules where an ultraviolet absorber is included therein.

(Prior Art)

It has been well known that ultraviolet ray has various influences to the skin.

Thus, ultraviolet ray of an UV-B region (290-320 nm) causes erythema and blisters on the skin and results in darkening of the skin after inflammation.

Although ultraviolet ray of an UV-A region (320-400 nm) does not generate erythema, it results in darkening of the skin

as same as in the case of the ultraviolet ray of an UV-B region.

In addition, ultraviolet ray causes a pigment sedimentation such as spots and freckles on the skin or results in aging and denaturation of the skin.

In order to solve such various problems, various ultraviolet absorbers have been developed already and have been contained in cosmetics for example.

Especially in the case of cosmetics, there is a big demand for shielding the ultraviolet ray from the skin and, accordingly, in addition to the above-mentioned ultraviolet absorbers (mainly that of an organic type such as p-aminobenzoate derivatives, benzotriazole derivatives, benzophenone derivatives and cinnamate derivatives), cosmetics which prevent the percutaneous absorption of ultraviolet ray by compounding with an inorganic pigment which is able to reflect the ultraviolet ray such as titanium dioxide and zinc oxide have been available in the market already.

(Problems to be Solved by the Invention)

(a) However, in the case of the cosmetics containing the above-mentioned ultraviolet absorbers of an organic type, the compatibility of the said ultraviolet absorbers with the cosmetic base and the feel in use are not always satisfactory.

In addition, when the cosmetic agent is applied to the skin, there is a problem that the ultraviolet absorber *per se* irritates the skin and further that, even when such an

ultraviolet absorber absorbs the optical energy, it gives a transient irritation to the skin.

Anyway, the cosmetics containing the conventional ultraviolet absorbers have any of the above-mentioned problems and, therefore, they are restricted to the specific types in practical application to the skin.

(b) On the other hand, in the case of the cosmetics containing the above-mentioned inorganic pigments, there is no problem in terms of irritation to the skin but, since they are not compounded with the cosmetics with an inherent object of ultraviolet absorbing effect, there are disadvantages that ultraviolet ray cannot be sufficiently shielded and that percutaneous absorption of the ultraviolet ray cannot be prevented.

Especially in the case of the cosmetics containing an inorganic pigment having a particle size of a region whereby visible light is shielded (where the particle size is relatively large), absorption of ultraviolet ray is weak.

On the contrary, in the case where fine particles of titanium dioxide are compounded, an effect of shielding the ultraviolet is achieved due to the light-scattering effect thereof but, due to the said scattering of the light, the skin shows a white and rising state. In addition, adhesion to the skin is bad and spreading ability is poor and, therefore, the cosmetic agent adheres to the skin with thickness whereby the

finish of the so-called makeup state lacks in transparency.

Anyway, up to now, there has been almost no development in the cosmetics which prevent the percutaneous absorption of ultraviolet ray and satisfy various requirements such as safety to the skin and compatibility.

The present invention has been carried out in order to solvent all of the above-mentioned problems and is to offer a cosmetic agent where absorbing and shielding effects of the ultraviolet ray which is harmful to the skin are good, percutaneous absorption of ultraviolet ray to the skin is prevented, safety and adhesion to and spreading ability on the skin are excellent, and both feel on actual use and transparency are excellent.

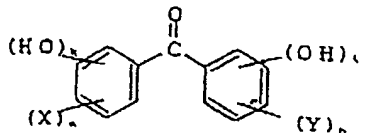
(Means to Solve the Problems)

The present inventors have carried out an intensive study for solving such problems and have found that, when a certain type of organic ultraviolet absorber is included in a certain type of inorganic spherical fine particles followed by making into microcapsules and they are compounded with a cosmetic agent, all of the above problems have been solved whereupon the present invention has been accomplished.

Thus, the present invention has been accomplished for solving the above problems and relates to microcapsules where an ultraviolet absorber is included therein, to a method for the manufacture of the said microcapsules, and to a cosmetic

agent containing the said microcapsules where an ultraviolet absorber is included therein.

Characteristic feature as the microcapsules is that a benzophenone derivative represented by the formula



(in the formula, X in the number of m and Y in the number of n each is same or different and each is a C_{1-24} alkyl group, alkoxy group, sulfonic acid group or an alkaline metal salt thereof; m and n each is an integer of 0-3; and the sum of k and l is an integer of 1-4) is included in spherical fine particles being mainly composed of silica and having an average particle size of 0.1-30μm.

The characteristic feature as a method for the manufacture of that microcapsules is that a benzophenone derivative represented by the above formula is dissolved in an aqueous solution of alkaline metal silicate, the aqueous solution is mixed with water and an organic solvent having a solubility of 5% or less to the above benzophenone derivative to prepare a water-in-oil type emulsion, then an acidic aqueous solution which is able to produce water-insoluble precipitate by a neutralization reaction of the above alkaline metal silicate and the benzophenone derivative dissolved in an alkali and, after that, filtration, washing with water and drying are carried out if necessary whereby the said benzophenone

derivative is included in spherical fine particles being mainly composed of silica and having an average particle size of 0.1-30 μm.

The characteristic feature as the cosmetic agent is that the microcapsules as mentioned above are compounded.

Examples of the benzophenone derivative represented by the above formula are as follows.

(a) 2,2'-dihydroxy-4-methoxybenzophenone;

(b) 2-hydroxy-4-methoxybenzophenone;

(c) 2-hydroxy-4-methoxybenzophenone-5-sulphonic acid;

(d) 2,2'-dihydroxy-4,4'-dimethoxybenzophenone;

(e) 2,2',4,4'-tetrahydroxybenzophenone;

(f) sodium 2,2'-dihydroxy-4,4'-dimethoxybenzophenone-5-sulphonate;

(g) 2,4-dihydroxybenzophenone;

(h) sodium 2-hydroxy-4-methoxybenzophenone-5-sulphonate;

(i) 2-hydroxy-4-octyloxybenzophenone;

(j) 2-hydroxy-4'-methoxybenzophenone;

(k) 2-hydroxybenzophenone;

(l) 4-hydroxybenzophenone;

(m) 2-hydroxy-4-methylbenzophenone;

(n) 2-hydroxy-5-methylbenzophenone;

(o) 2,5-dihydroxybenzophenone; and

(p) 2-hydroxy-5-methoxybenzophenone.

However, the kind of the benzophenone derivative in the present invention is not limited to the above-mentioned (a)-(p) only.

In the method for the manufacture of the above microcapsules of the present invention, examples of the alkaline metal silicate used therefor are sodium silicate of JIS No.1, sodium silicate of JIS No.2, sodium silicate of JIS No.3, sodium metasilicate and potassium silicate ($K_2O.nSiO_2$ where n is 2~3.8).

Examples of the organic solvent used in the above manufacturing method are aliphatic saturated hydrocarbons such as n-hexane, decane and octane; aromatic hydrocarbons such as toluene, benzene and xylene; and alicyclic hydrocarbons such as cyclohexane.

Each of those solvents may be used solely or two or more of them may be used jointly.

As to an emulsifier used for the said manufacturing method, a nonionic surface-active agent having an HLB of within a range of preferably 3.5-6.0 may be used. Representative examples are sorbitan sesquioleate, sorbitan monooleate and polyoxyethylene sorbitan trioleate.

Preferred examples of the acidic aqueous solution used in the said manufacturing method are those which contain multi-charged anion such as sulfate ion and phosphate ion. For example, when the above benzophenone derivative is 2,4-

dihydroxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxy-benzopheone, 2,2',4,4'-tetrahydroxybenzophenone, etc., an acidic aqueous solution where the pH after completion of the reaction is 5 or lower or, particularly, 3 or lower is preferred. Incidentally, the higher the concentration, the better.

Types of the alkaline silicate, the organic solvent, the emulsifier and the acidic aqueous solution are not limited to those which are mentioned hereinabove.

(Function)

(1) Concerning the preparation mechanism

Fig. 1 is an illustrative drawing which shows the production process of the fine particles of the microcapsule of the present invention.

First, a benzophenone derivative is dissolved in an aqueous solution of alkaline metal silicate and the resulting aqueous solution is mixed with an organic solvent to prepare, as shown in (a) of Fig. 1, an emulsion of water-in-oil type where the above mixed solution of the benzophenone derivative and the alkaline metal silicate is a dispersoid 1 while the organic solvent is a dispersoid 2.

Then the said emulsion is mixed with the above acidic aqueous solution.

At that time, the following chemical reaction takes place at the interface of the above dispersoid 1 and the acidic aqueous solution.

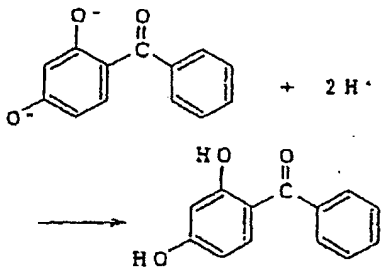
(a) $SiO_3^{2-} + 2H^+ \rightarrow SiO_2 + H_2O$

($Si_2O_5^{2-} + 2H^+ \rightarrow 2SiO_2 + H_2O$)

and (b) $R\text{-}O^- + H^+ \rightarrow R\text{-}OH$

(where R is a benzophenone skeleton)

Incidentally, when R is 2,4-dihydroxybenzophenone for example, this reaction (b) is as follows.



The chemical reaction at the interface in the present invention proceeds in such a manner as in the above reaction formulae and is a co-precipitation reaction where those two chemical reactions proceed simultaneously.

However, in terms of the reaction rate, the reaction (a) proceeds quicker than the reaction (b) and, therefore, a thin film (3) of silica is firstly formed at the above interface and then, with a lapse of time, the interface reaction proceeds in the inner side of the internal aqueous phase whereupon the microcapsules (5) are manufactured where the product (4) of the benzophenone is included in the silica.

(2) Prevention of elution of the included benzophenone derivative

A large amount of adhered water is contained in the microcapsules where the benzophenone derivative is included in the spherical fine particles mainly consisting of silica prepared in the above reaction mechanism and, therefore, it is preferred to heat at a high temperature of 100°C or higher within such an extent that the benzophenone is not deteriorated. As a result of such an operation, elution of the included benzophenone can be suppressed as much as possible.

It is also possible that, after that, a known surface treatment such as a treatment with silicone oil is carried out whereby elution of the included benzophenone derivative can be suppressed.

(Examples)

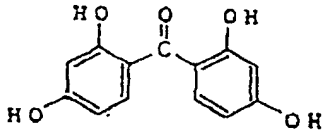
Examples of the present invention will be illustrated as hereinafter.

[Examples for the manufacture of microcapsules]

Example 1.

This is an example for the microcapsules where 2,2',4,4'-tetrahydroxybenzophenone which is an example of the benzophenone derivative of the present invention is included.

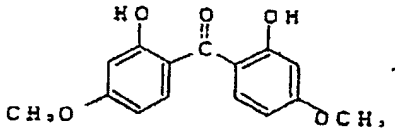
Thus, the microcapsules in this example are constructed by including 18.22% by weight of 2,2',4,4'-tetrahydroxybenzophoenone having the following formula in the spherical fine particles mainly consisting of silica and the average particle size thereof is 1.8μm.



Example 2.

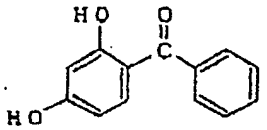
This is an example for the microcapsules where 2,2'-dihydroxy-4,4'-dimethoxybenzophenone which is an example of the benzophenone derivative of the present invention is included.

Thus, the microcapsules in this example are constructed by including 22.04% by weight of 2,2'-dihydroxy-4,4'-dimethoxybenzophoenone having the following formula in the spherical fine particles mainly consisting of silica and the average particle size thereof is 2.2μm.



Example 3.

This is an example for the microcapsules where 2,4-dihydroxybenzophenone which is an example of the benzophenone derivative of the present invention is included.



Thus, the microcapsules in this example are constructed by including 19.5% by weight of 2,4-dihydroxybenzophoenone

having the above formula in the spherical fine particles mainly consisting of silica and the average particle size thereof is 3.1 μm.

Incidentally, the particle size of the microcapsules of the present invention is not limited to those mentioned in the above Examples and the important thing is that an average particle size of the spherical fine particles constituting the said microcapsules is formed in 0.1-30 μm.

Referential Example.

Ultraviolet absorption spectra of the microcapsules of the above Examples 1-3 were measured and a test for a slip abrasion was carried out as well.

(1) Ultraviolet absorption spectrum

The sample powder of each of the above Examples was added to white vaseline (Japanese Pharmacopoeia) to an extent of 20% by weight, dispersed by means of well kneading and applied between quartz plates to make the thickness 15 μm and its ultraviolet absorption spectrum was measured.

The result was that, as shown in Fig. 3, the microcapsules of each of the above Examples showed the absorption spectrum corresponding to the ultraviolet absorption spectrum of the included benzophenone derivative and a sufficient ultraviolet absorbing ability is shown to the ultraviolet ray of UV-A or UV-B region which is a problem in association with the percutaneous absorption.

(2) Slip abrasion

The sample in each of the above Examples was thinly applied onto a glass plate and, when a flat glass plate on which a weight of 200 g was put was placed thereon and pulled in a horizontal direction, the strength of the force at the sliding stage was measured and its relative value is shown by a bar graph in Fig. 4.

As a result, it has been found that the slip abrasion was small as compared with talc, sericite, red iron oxide and titanium oxide which are contained in the common cosmetics.

This is presumably because, since the microcapsules are in a really spherical shape, a rolling effect (a tumbling property) is good as compared with the above-mentioned talc, etc.

[Examples of the method for the manufacture of microcapsules]

Example 4.

This is an example of a method for the manufacture of microcapsules in which 2,2',4,4'-tetrahydroxybenzophenone of the above Example 1 is included.

Firstly, 4.05 g of 2,2',4,4'-tetrahydroxybenzophenone were dissolved in 90 ml of a 1.5 mol/liter solution of sodium silicate No.1, then the aqueous solution was poured over 150 ml of a mixture of sorbitan sesquioleate and polyoxyethylene sorbitan trioleate (mixing ratio being 4:1) and the mixture was emulsified for five minutes using a homomixer to prepare

an emulsion of a water-in-oil type.

Then, the emulsion was poured over 450 ml of a mixed aqueous solution of 1.2 mol/liter of ammonium sulfate, 0.88 mol/liter of sodium dihydrogen phosphate and 0.72 mol/liter of phosphoric acid and the mixture was stirred for one hour and allowed to stand for one night. After that, it was centrifuged to separate into solid and liquid and the solid was filtered, washed with water and dried at 120°C.

As a result, 19.7 g of microcapsules of an average particle size of 1.8 μm where 18.22% by weight of 2,2',4,4'-tetrahydroxybenzophenone were included in spherical fine particles mainly consisting of silica were prepared.

When the microcapsules of this Example were observed under a scanning electron microscope, they were found to be really spherical as in Fig. 2.

Example 5.

This is an example of a method for the manufacture of microcapsules in which 2,2'-dihydroxy-4,4'-dimethoxybenzophenone which is an example of the benzophenone derivative of the present invention is included.

Firstly, 13.5 g of 2,2'-dihydroxy-4,4'-dimethoxybenzophenone were dissolved in 225 ml of a 1.5 mol/liter solution of sodium silicate No.1, then the aqueous solution was poured over 400 ml of a mixture of sorbitan

sesquioleate and polyoxyethylene sorbitan trioleate (mixing ratio being 3:1) and the mixture was emulsified for five minutes using a homomixer to prepare an emulsion of a water-in-oil type.

Then, the emulsion was poured over 1200 ml of a mixed aqueous solution of 1.5 mol/liter of ammonium sulfate, 0.75 mol/liter of sodium dihydrogen phosphate and 0.75 mol/liter of phosphoric acid and the mixture was stirred for one hour and allowed to stand for 12 hours. After that, the same operation as in the above Example 4 was carried out to give 50.7 g of microcapsules of an average particle size of 2.2 μ m where 22.04% by weight of 2,2'-dihydroxy-4,4'-dimethoxybenzophenone were included in spherical fine particles mainly consisting of silica.

Example 6.

This is an example of a method for the manufacture of microcapsules in which 2,4-dihydroxybenzophenone which is an example of the benzophenone derivative of the present invention is included.

Firstly, 10.0 g of 2,4-dihydroxybenzophenone were dissolved in 200 ml of a 1.5 mol/liter solution of sodium silicate No.1, then the aqueous solution was poured over 350 ml of a 5% solution of mixture of sorbitan monooleate and polyoxyethylene sorbitan monooleate (mixing ratio being 6:1) in n-hexane and the mixture was emulsified for three minutes using a homomixer to prepare an emulsion of a water-in-oil type.

Then, the emulsion was poured over 1000 ml of a mixed aqueous solution of 1.2 mol/liter of sodium dihydrogen phosphate and 1.8 mol/liter of phosphoric acid and the mixture was stirred for one hour and allowed to stand for one night. After that, the same operation as in the above Example 4 was carried out to give 45.2 g of microcapsules of an average particle size of 3.1 μm where 19.52% by weight of 2,4-dihydroxybenzophenone were included in spherical fine particles mainly consisting of silica.

[Examples for cosmetics]

The microcapsules as such can be compounded with cosmetics, pharmaceuticals, etc. with an object of preventing the bad affection of ultraviolet ray to the skin.

The compounding amount of the microcapsules in cosmetics may vary depending upon the type of the cosmetics but, usually, it is preferred to compound so as to make 0.1-20% by weight or, particularly, 0.5-10% by weight as a benzophenone derivative.

The cosmetic agent of the present invention can be prepared by compounding the microcapsules as such with the known cosmetic base by a conventional method to make into various forms such as cream, solution, stick, milky lotion, foundation and ointment.

Thus, the microcapsules as such are selected and used depending upon the cosmetic base whereby it is now possible

to manufacture the cosmetics of various forms having an ultraviolet absorbing effect such as a base cosmetics (e.g., a cosmetic oil containing an oily base, an oily cream or oily milky lotion where a lot of oily base is compounded, an weakly oily cream or weakly oily milky lotion where a lot of water is compounded, and a water-based cosmetic lotion) and various makeup cosmetics using an oily agent as a base (e.g. foundation and lipstick).

Now, the examples of the cosmetics of the present invention will be given as hereunder.

Example 7.

This is an example of the cosmetics where the microcapsules of the present invention are compounded with the so-called powder foundation.

Thus, the composition of the cosmetic agent of this Example is as follows.

Component	% by Weight
(1) Microcapsules of Example 1	30.0
(2) Talc	balance
(3) Mica	30.0
(4) Mica titanium	1.0
(5) Titanium oxide	8.0
(6) Red iron oxide	0.7
(7) Yellow iron oxide	1.8
(8) Black iron oxide	0.2

(9) Crystalline cellulose	0.2
(10) Methyl polysiloxane	4.0
(11) Squalane	4.0
(12) Perfume	q.s.
(13) Antiseptic and antioxidant	a little

In the manufacture of the cosmetic agent of this Example, the above (1)-(9) were well stirred using a Henschel mixer together with a uniform addition of other components thereto and the mixture was treated with a grinding machine and molded by compression.

The cosmetic agent of this Example showed a transparent feel and an adhesive property and was able to be adhered to the skin in a thin and uniform manner.

It was also noted that the effect of shielding the ultraviolet ray was very high.

In addition, unlike the conventional cosmetics compounded with inorganic pigments, there was no rise of white color from the skin.

Further, a soft feel in use was available and the sustained property of the cosmetics was good as well.

Example 8.

This is an example of the cosmetics where the microcapsules of the present invention are compounded with a foundation of a water-in-oil emulsified type.

Thus, the composition of the cosmetic agent of this

Example is as follows.

Component	% by Weight
(1) Microcapsules of Example 2	10.0
(2) Microcapsules of Example 3	10.0
(3) Titanium Oxide	8.0
(4) Kaolin	2.0
(5) Talc	5.0
(6) Solid paraffin	5.0
(7) Lanolin	10.0
(8) Liquid paraffin	27.0
(9) Sorbitan sesquioleate	5.0
(10) Pure water	balance
(11) Perfume	q.s.
(12) Antiseptic and antioxidant	a little

In the manufacture of the cosmetic agent of this Example, the above (1)-(5) were mixed firstly and treated with a grinding machine to give powder. To this powder were added a part of (8) and (9), the mixture was homogeneously dispersed using a homomixer, other components except (10) which were melted by heating were added thereto and the mixture was kept at 70°C (oily phase). After that, (10) was heated at 70°C and added to the oily phase, the mixture was homogeneously emulsified and dispersed using a homomixer and, after emulsification, it was cooled down to 40°C with stirring.

The cosmetic agent of this Example had a high shielding

effect to ultraviolet ray and showed excellent feel on use and transparent feel.

In addition, its effect of preventing a rise of white color on the skin was excellent and the sustained property of the cosmetics was good as well.

Example 9.

This is an example of the cosmetics where the microcapsules of the present invention are compounded with a cream of a water-in-oil type.

Thus, the composition of the cosmetic agent of this Example is as follows.

Component	% by Weight
(1) Microcrystalline wax	11.0
(2) Beeswax	4.0
(3) Vaseline	6.0
(4) Solid paraffin	5.0
(5) Squalane	30.0
(6) Hexadecyl adipate	10.0
(7) Glycerol monooleate	3.0
(8) Polyoxyethylene(20) sorbitan oleate	1.0
(9) Propylene glycol	2.5
(10) Microcapsules of Example 1	10.0
(11) Pure water	balance
(12) Perfume	q.s.
(13) Antiseptic and antioxidant	a little

In the manufacture of the cosmetic agent of this Example, (9) and (10) were firstly to (11) and the mixture was heated and kept at 80℃ (aqueous phase). In the meanwhile, other components were mixed and heated, melted and kept at 80℃ (oily phase). (10) in the aqueous phase was homogeneously dispersed using a homomixer, then the aqueous phase was added to the oily phase, the mixture was homogeneously emulsified using a homomixer and, after that emulsification, it was stirred with cooling to give the cosmetic agent.

The cosmetic agent of this Example showed an excellent shielding effect to ultraviolet ray and was with higher safety than the conventional cosmetics.

In addition, it adheres to the skin in a thin and uniform manner, has a closely adhering property and, further, its feel on use and transparent feel are excellent.

In addition, there was no rise of white color and the sustained property of the cosmetic agent was good as well.

Example 10.

This is an example where the microcapsules of the present invention was compounded with a cream of an oil-in-water type.

Thus, the composition of the cosmetic agent of this Example is as follows.

Component	% by Weight
(1) Beeswax	10.0
(2) Cetyl alcohol	5.0

(3) Hydrogenated lanolin	8.0
(4) Squalane	32.5
(5) Glycerol monostearate	2.0
(6) Polyoxyethylene(20) sorbitan monolaurate	2.0
(7) 1,3-Butylene glycol	5.0
(8) Microcapsules of Example 2	10.0
(9) Pure water	balance
(10) Perfume	q.s.
(11) Antiseptic and antioxidant	a little

In the manufacture of the cosmetic agent of this Example, (7) and (8) were firstly to (9) and the mixture was heated and kept at 70 ℃ (aqueous phase). In the meanwhile, other components were mixed and heated, melted and kept at 70℃ (oily phase). (8) in the aqueous phase was homogeneously dispersed using a homomixer, then the aqueous phase was added to the oily phase, the mixture was homogeneously emulsified using a homomixer and, after that emulsification, it was stirred with cooling to give the cosmetic agent.

The cosmetic agent of this Example showed an excellent shielding effect to ultraviolet ray and was with higher safety than the conventional cosmetics.

In addition, it adheres to the skin in a thin and uniform manner, has a closely adhering property and, further, its feel on use and transparent feel are excellent.

In addition, there was no rise of white color and the

sustained property of the cosmetic agent was good as well.

Example 11.

This is an example for a cosmetic agent where the microcapsules of the present invention was compounded with a milky lotion.

Thus, the composition of this Example is as follows.

Component	% by Weight
(1) Stearic acid	2.5
(2) Cetyl alcohol	1.5
(3) Vaseline	5.0
(4) Liquid paraffin	10.0
(5) Polyoxyethylene(10) monooleate	2.0
(6) Polyethylene glycol 1500	3.0
(7) Triethanolamine	2.0
(8) Carboxyvinyl polymer	0.15
(9) Microcapsules of Example 3	10.0
(10) Pure water	balance
(11) Perfume	q.s.
(12) Antiseptic and antioxidant	a little

In the manufacture of the cosmetic agent of this Example, (6) to (9) were firstly to (10) and the mixture was heated and kept at 80 ℃ (aqueous phase). In the meanwhile, other components were mixed and heated, melted and kept at 80℃ (oily phase). (9) in the aqueous phase was homogeneously dispersed using a homomixer, then the aqueous phase was added to the oily

phase, the mixture was homogeneously emulsified using a homomixer and, after that emulsification, it was stirred with cooling at 30℃ to give the cosmetic agent.

The cosmetic agent of this Example showed an excellent shielding effect to ultraviolet ray and was with higher safety than the conventional cosmetics.

In addition, it adheres to the skin in a thin and uniform manner, has a closely adhering property and, further, its feel on use and transparent feel are excellent.

In addition, there was no rise of white color and the sustained property of the cosmetic agent was good as well.

Example 12.

This is an example for a cosmetic agent where the microcapsules of the present invention were compounded with a lip cream.

Thus, the composition of the cosmetic agent of this Example is as follows.

Component	% by Weight
(1) Microcapsules of Example 2	3.0
(2) Microcapsules of Example 3	4.0
(3) Candelilla wax	2.9
(4) Ceresin	14.9
(5) Resina	4.8
(6) Octyldodecanol	7.0
(7) Diisostearate	35.5

(8) Glycerol tri-2-ethylhexanoate	22.2
(9) Neopentylglycol dioctanoate	5.6
(10) Perfume	q.s.
(11) Antisepetic and antioxidant	a little

In the manufacture of the cosmetic agent of this Example, (1) and (2) were firstly added to a part of (7) and the mixture was treated with a three-roller machine to prepare a pigment part. Then other components were mixed and heated to melt, the above pigment part was added thereto and the mixture was homogeneously dispersed using a homomixer. After being dispersed, it was poured into a mold and quickly cooled and the resulting sticks were inserted into containers and subjected to a framing. As such, the cosmetic agent was prepared.

The cosmetic agent of this Example has an excellent shielding effect to ultraviolet ray and has a high safety as compared with the conventional cosmetics.

Further, it adheres to the lip in a thin and uniform manner and, moreover, it has excellent feel on use and transparent feel.

Furthermore, it shows a good sustained cosmetic effect.

(Advantages of the Invention)

(a) A mentioned above, the microcapsules of the present invention are in such a constitution that a benzophenone derivative which is an ultraviolet absorber is included in

spherical fine particles of an average particle size of 0.1-30 μm mainly consisting of silica. Therefore, they have significant advantages that the ultraviolet absorber does not directly contact to the skin whereby the irritation to the skin can be reduced and such a safety is significantly enhanced as compared with the conventional ultraviolet absorbers.

Accordingly, there are advantages that the cosmetic agent in which such microcapsules are contained also exhibits an effect of mitigating the irritation to the skin.

(b) In addition, the microcapsules themselves are powdery and, therefore, there is an advantage that they can be easily compounded with the cosmetic base with which compounding of the conventional ultraviolet absorber has been difficult.

(c) Further, the microcapsules are in really spherical powders and, accordingly, there are advantages that the spreading ability of the cosmetics containing such microcapsules is very good as compared with the conventional cosmetics containing inorganic pigments and that the cosmetics do not thickly adhere to the skin but adhere in a thin and uniform manner whereby their load to the skin is small.

(d) Furthermore, in such cosmetics, the spherical fine particles constituting the outer walls of the microcapsules contained therein are composed of silica having a refractive index to light which is nearly the same that of the oily solvent

in the cosmetic base. Therefore, there is an advantage that, unlike the conventional cosmetics containing titanium oxide, they do not give an impression as if the skin rises in white color due to diffraction of light.

(e) Moreover, the cosmetics of the present invention has an advantage that the transparent feel is good, charging property with pressure is good and the sustained cosmetic effect is satisfactory.

(f) Still further, in the method for the manufacture in accordance with the present invention, a benzophenone derivative is dissolved in an aqueous solution of an alkaline metal silicate, the said aqueous solution is mixed with an organic solvent to prepare an emulsion of a water-in-oil type and then an acidic aqueous solution which is able to produce a water-insoluble precipitate by a neutralization reaction of the above alkaline metal silicate and the benzophenone derivative dissolved in an alkali is mixed with the above emulsion. Consequently, the said benzophenone derivative is included in the spherical fine particles mainly composed of silica to give the microcapsules.

Particularly in the following co-precipitating reactions at the interface, i.e.

(a) $SiO_3^{2-} + 2H^+ \rightarrow SiO_2 + H_2O$

$(Si_2O_5^{2-} + 2H^+ \rightarrow 2SiO_2 + H_2O)$

and (b) $R\text{-}O^- + H^+ \rightarrow R\text{-}OH$

(where R is a benzophenone skeleton), the reaction (a) proceeds quicker than the reaction (b) and, therefore, the benzophenone derivative is surely included in the spherical fine particles whereby there is an advantage that the manufacture of the microcapsules can be surely carried out.

Brief Explanation of the Drawings:

Fig. 1 is an illustrative drawing which shows the manufacturing process of the microcapsules.

Fig. 2 is an enlarged picture of the microcapsules in one of the Examples under a scanning electron microscope.

Fig. 3 is a chart of the ultraviolet absorption spectrum of the microcapsules in one of the Examples.

Fig. 4 is a graph which shows the slip abrasion test of the microcapsules in one of the Examples.

(Amendment submitted as of October 26, 1988)

The sentence reading "Fig. 2 is ..... microscope." in lines 10-11, page 30 (of the translation) is cancelled.

"Fig. 3" in lines 12-13, page 30 (of the translation) is amended to read -- Fig. 2 --.

"Fig. 4" in lines 14-15, page 30 (of the translation) is amended to read -- Fig. 3 --.

The attached Fig. 1 to Fig. 3 are amended to those which are attached herewith.

Fig. 4 is cancelled.

(Translation of the sentences in the drawings is given below for the new Figs. 1-3 amended as such - Translator)

Fig. 1

upper left: (a)

upper right: (b)

lower: (c)

Fig. 2

ordinate: Absorbance

abscissa: Wave Length (nm)

A: Microcapsules of Example 1

B: Microcapsules of Example 2

C: Microcapsules of Example 3

D: Spherical fine particles of silica (average particles size being 1.8μm)

E: Talc

Solid concentration: 20 wt%

Dispersing medium: white vaseline

Thickness of sample: 15 μ m (sandwiched between quartz plates)

Fig. 3

(in the order of from upper to bottom)

A

B

C

Talc

Sericite

Titanium oxide

Red iron oxide

Nylon powder

A: Microcapsules of Example 1

B: Microcapsules of Example 2

C: Microcapsules of Example 3

(Amendment submitted as of September , 1989) (date illegible - Translator)

The term "percutaneous absorption" (line 14, page 4; line 13, page 5; line 3, page 6; line 10, page 6; and line 25, page 14 of the translation) is amended to read -- irradiation to skin --.